THE CHARACTERISTICS OF BANK-FILTRATION AQUIFERS

by

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Abstract

Nowadays special rock sampling enables us to take comparatively full samples from riverbank-filtration aquifers. These samples will contain the silt fraction of gravelly sand, which is most influencing on the chemical character of the ground-water concerned. Analytical data bearing on the chemical, mineralogical and mechanical features of the silt fraction show the distribution in space of the hydrochemical characteristics. This could not be attained to when dealing only with the gravel and sand components of the aquiferous rock.

Examining and comparing the quality and quantity of the silt fraction with the favourable and unfavourable chemical properties of water stored in two bank-filtration aquifers along the river Danube, a definite relation could be found between them, by means of which the water quality can be predicted for a long time.

Introduction

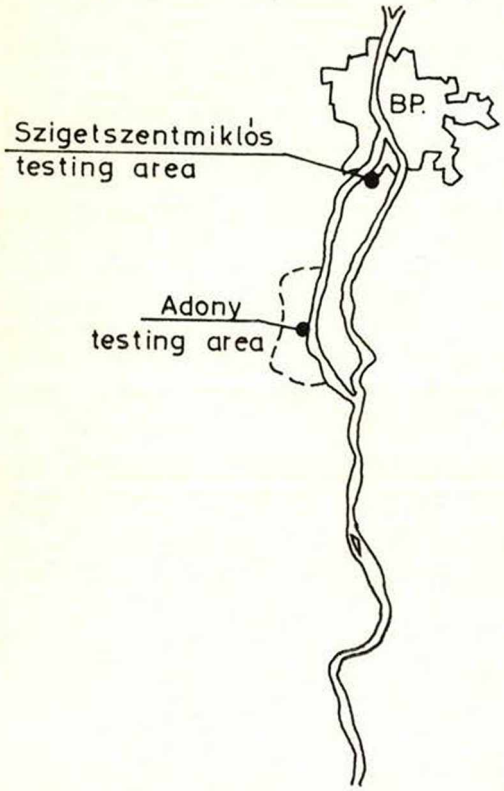
When drilling producing or observation wells with the usual method, the silt fraction, that is most likely to determine the chemical properties of water, leak away while taking out samples. Thus we will get only the gravel and sand fraction. That is why there is no correlation between the spatial differences of water-chemical properties and the chemical and mineralogical-lithological properties of the gravel-sand samples in bank-filtration aquifers.

Since there are also other factors controlling the chemical properties of water (e. g. operational conditions by production or pumping tests, the morphology of the underlying impervious rock surface, the thickness of the water-bearing bed, different kinds of impact from the ground surface etc.), all effects not related to rock quality have been put in correction.

We examined two sites along the Danube; the first one is between km marks 1593 and 1612 on the right side, while the second is between km marks 1632 and 1633 on the left side *(Fig. 1.)*. We can find areas with and without water production on either site.

Localization of investigated territories

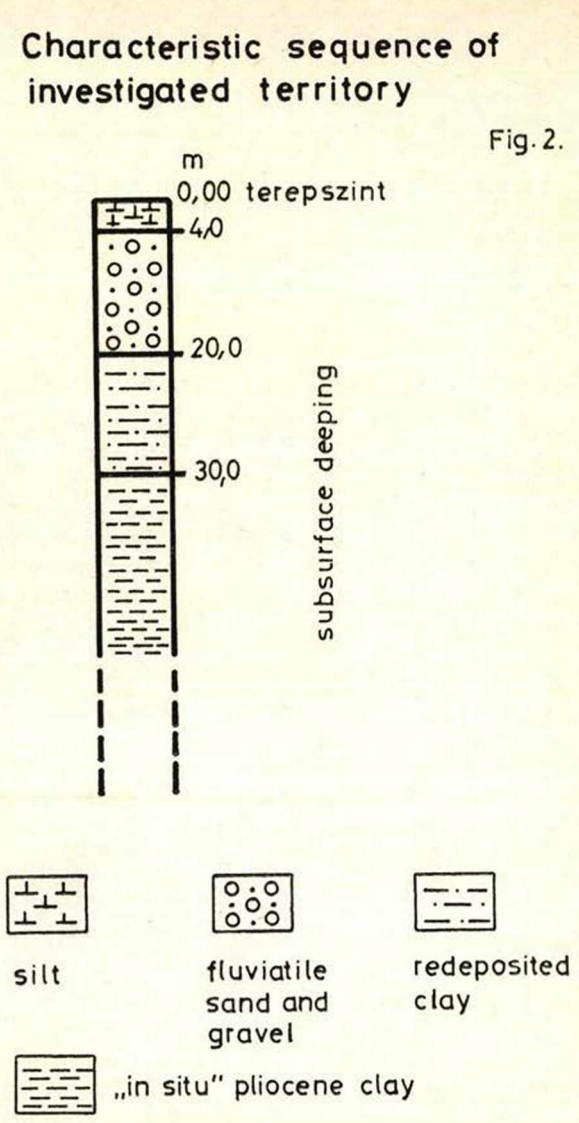
Fig. 1.



The geological – hydrogeological description of the test sites

The oldest formation we examined was a clay deposited within hyposaline environment and assigned to the Middle Pannonian Stage (*Congeria ungula caprae* biozone). However, this clay of brackish-water deposition can only be found as autochtonous in the deeper horizons. We could observe in the test sites that due to soaking the upper part of the clay have become loose and turned out to be redeposited by river erosion *(Fig. 2.)*. That resedimentation is verifiable upon the following considerations:

a) The bedding is different from that of the Pannonian deposits. In the vicinity of the Pannonian inland water basin the rhythmicity of stratifi-



cation falls between 10^{-1} and 10^{0} m, while in the resedimented sequence it varies between 10^{-3} and 10^{-2} m. Anyway, there are also signs of crossbedding on core samples.

b) Characteristically coarse-grained accessory materials are present in sand and gravel lenses of lamellar bedding.

Since the material is the same as that of the Pannonian clay (apart from the accessory sand and gravel parts), it also contains the same mine-

rals and chemical components. Iron-sulphide is the most important of them. It appears as pyrite or marcasite in a crystallized form (FeS_2) and as colloidal melnikovite or hydrotroilite ($FeS_{1-2} \cdot nH_2O$) in its less crystallized form. None of these are stable under oxidizing conditions. Being oxidized they turn to be ferrioxihydroxide and sulphuric acid. This sulphuric acid reacts with the Ca – Mg carbonates "in statu nascendi", thus forming poorly watersoluble $CaSO_4 \cdot nH_2O$ (gypsum) and well soluble $MgSO_4 \cdot nH_2O$ I washed out and centrifuged the microscopic and submicroscopic crystals of gypsum found in the underlying layer. The $MgSO_4$ solvent migrates upwards to the water-bearing layer and increases its hardness and sulphate content. As gypsum is poorly soluble in water (2.6 g/l at ground water temperature), it serves as a potential calcium and sulphate pollutant for longer periods of time. The solubility of dolomite is 0.3 g/l, that of the calcite is 0.1 g/l so we can assume that the high degree of water hardness in the underlying bed is mainly due to processes starting with the oxidation of the pyrite. Because of the present sulphate concentration the clay minerals change their structure; montmorillonite turns into kaolinite. We could reveal this process - already well known from the mineralogical literature - by means of direct X-ray examination and indirect ion-exchanger absorption capacity measurements (The ion-exchanger absorption capacity of the primary Pannonian clay is 40 – 60 mekv/100g, and that on the upper part of the redeposited sequence is 27 – 29 mekv/100g) *(Fig. 3.)*.

The grain size in the water-bearing gravel and sand mixture is varied *(Fig. 4.)*. The mixture also contains the mud fraction coming from the suspension load of the original sedimentary basin, but we could not examine this fraction because of adopting the usual drilling method. The sandy gravel belongs to Terrace System 2/b of the Late Holocene. Its material is dominated by metamorphic quartzite, eroded from the Tauern-Alps. Quartzite is chemically indifferent for ground water, it gains importance only because of its incrustration. On higher reliefs congelational incrusting is characteristic, limonite (FeO/OH), and pyrolusite (δMnO_2) form chemosorbtional surfaces. I could not find any congelation crusts in the examined River Terrace 2/b.

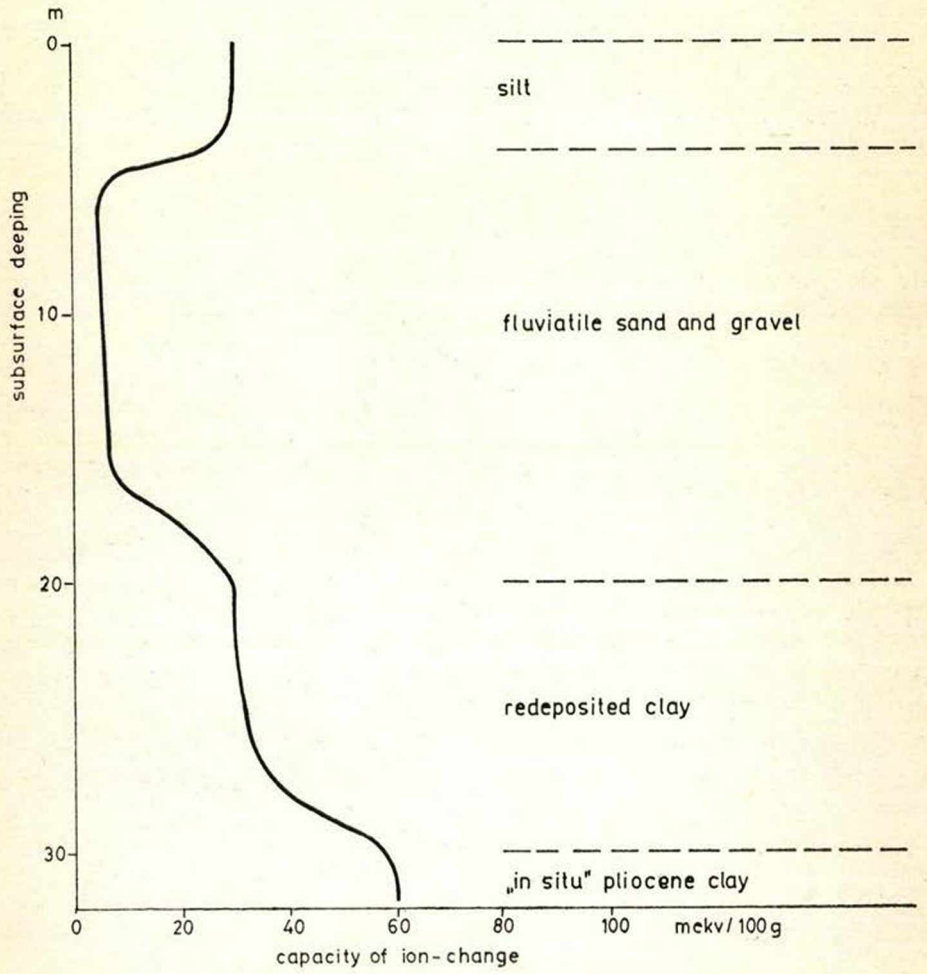
The oxidation – precipitated ferrioxihydroxide coatings are mainly in colloidal phase and hardly mineralizated at all, therefore they are reversible and easily pass into solution for reductive or acidic effects.

Manganese does not form coatings by oxidation, because the actual redox potential of the bank-filtration aquifer (+150 – +450mV) is smaller than the reduced normal redox potential of the manganese. The quantity of the ferrioxihydroxide coat depends on the extension of the specific surface; the smaller the grain size is, the bigger it gets. This is the primary, water-chemical effect of grain distribution.

The small amount of andesite grains on the gravel and sand fraction is strongly weathered and still keeps on weathering. We investigated this process earlier because the technical literature presumed that ions are to be lost during weathering. As a result of a profound investigation we realized that the potential amount of the released iron and manganese is so small

Relation between capacity of ion-change and deeping

Fig. 3.

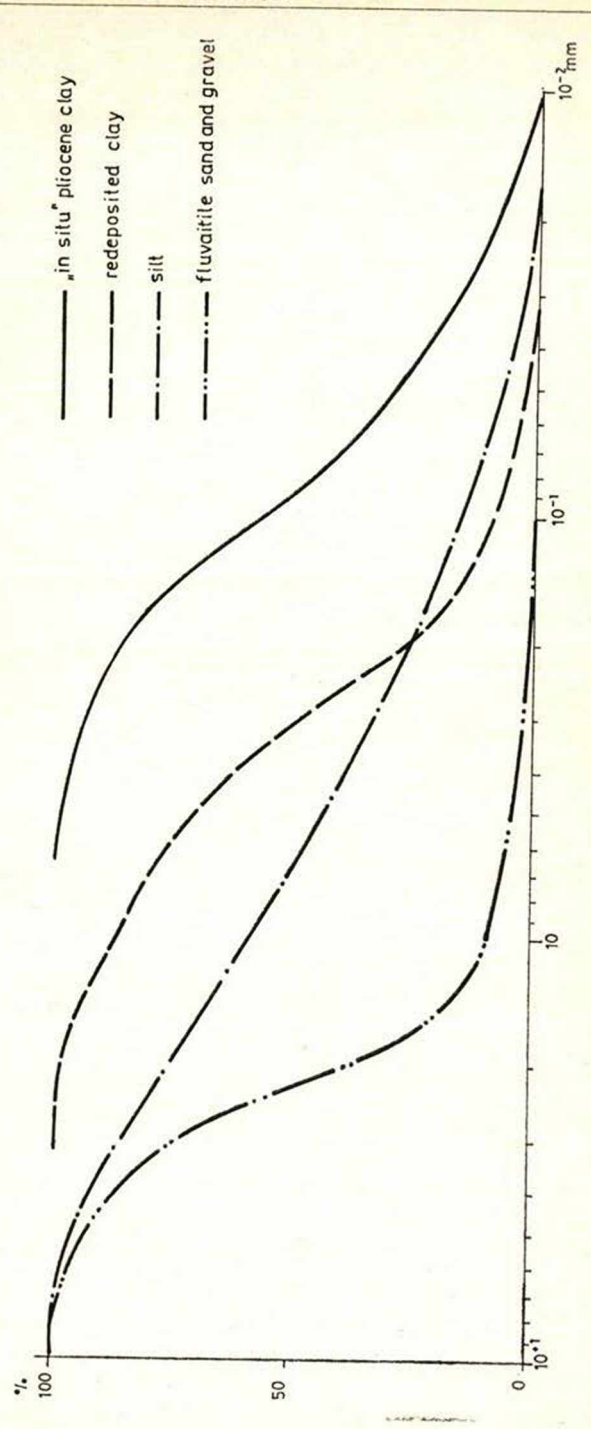


that it can be neglected, the ion concentration of the solution due to slow weathering is insignificant. We are not going to doubt the importance of the released ions (mainly Fe, Mn, K, Na) in the primary accumulation but in the case of recent processes we can neglect them.

Among the grains we can also find dolomite and limestone grains of any size, in less than 0.1 percent. Chemically they act similarly to the carbonates of the underlying bed already discussed, that is, they neutralize

Fig. 4.

Typical granulometric composition of investigated geological formations



acids. Both the calcium and the magnesium reacts with sulphate; gypsum is formed in the first case and water soluble salts in the other. However, the solubility of the original carbonate is not known because the underground water is much less saturated than the theoretical solubility of the carbonates would indicate and in addition we could not observe a considerable degree of solution on the pebbles, neither under natural conditions nor in laboratory. Comparing this with the solubility of artificial limestone and dolomite grains of the similar size this difference is very remarkable. Therefore we presume but cannot substantiate that either an alkalophillic and chemolithotrophic bacterium culture appears around the carbonate grains in bank-filtration aquifers or the humic acid forms chelate-complex with the calcium, thus serving as a protective colloid.

The most important fraction of the reservoir is the silt-fraction. According to the practice of engineering geology we separated it with rinsing by means of a sieve with 20 μm meshes (sieve standard Fritsch Afnor NFX 11–501. No 14.) but also examined the 20–50 μm fraction if it turned out to be useful in some way.

The silt content of the sandy gravel can be of different origin. Recent colmatation can be observed in the vicinity of the present riverbed and fossil colmatation near the fossil one. As our previous investigation of different purpose showed, the colmatated layer is very thin, n. 0.1 m, max. 1.5 m. This was revealed in several places along the Danube by means of drillings along recent and fossil riverbeds and hoeing along the bank. In this article we do not intend to go into details concerning this problem, just mention that – according to our investigation – the change in the quality of the water, filtering from the Danube, is obviously in connection with the colmatated layer and its dwelling time has less importance than the special literature presumes.

The more or less evenly dispersed silt content of the reservoir is syngenetic and originates from the suspension matter content of the sedimentary substance of the gravelly sand of the fossil river. This seems to contradict the principles of sedimentation which states that different fractions would have to separate (gravel and sand as well as mud), yet it is very well known from our experience that this can be seen neither in recent nor in fossil deposits, probably because it is covered by the dinamics of slurry movement.

We examined the suspended matter content of the Danube. The chemical compound of the filtered and rinsed (ie free of soluted salts) dry matters are the followings:

SiO_2	8.8%
Al_2O_3	4.9%
Fe_2O_3	0.4%
CaO	14.3%
MgO	2.9%
Na_2O	9.8%
K_2O	2.1%

Cl^-	6.4%
SO_4^{2-}	12.3%
ignition losses:	38 %
	99.9%

(Note: At about two third of the ignition losses is C-org and one third is CO_2)

A considerable part of the ignition losses is detritus which reacts very quickly for H_2O_2 treatment. Chemical oxygen demand (COD) measurement gave the proportions mentioned above, after the extraction of the carbonates.

The concentration and compound of the suspended matters in the Danube change according to the water level and cause small deviations from those in the silt-fraction of the reservoir.

The ion-exchanger absorption capacity of the clay minerals is estimated to be as common but cannot be measured properly because it can hardly be separated from the other components, and because the bearing materials of the organic matters also have surface activity and absorption.

By means of X-ray examination we could see, that the compound of the clay minerals is varied and on an average contains 50 percent of montmorillonite, 20 percent of kaolinite and 30 percent of illite.

We can not measure at what rate is montmorillonite able to react with organic matters since it cannot be separated with the available methods, therefore, we presumed that clay-minerals and detritus form their absorptive systems separately. (Otherwise the two systems would neutralize each other, thus making absorption impossible.) Indirect measurements made our presumption plausible.

The surface activity of the suspended matters have two effects. It assists some chemical processes (mainly reductive ones), and accumulates the produced materials on the surface while making the activities of bacteria possible at the same time. The environmental conditions, needed for the optimal life-functions of these bacteria does not meet the actual environmental conditions; they could find stable micro-conditions (pH, pE, etc.) for their survival only in the silty nodes, where the low speed of current and diffusion (due to bad fluid transmission) does not keep up the balance between the different chemical environments.

Overlying formations

The overlying bed of the reservoir is alluvial clay. Depending on its sand content it is either bound or friable. Our permeameter has shown a high vertical conductivity ($1.2 \cdot 10^{-6} - 4.9 \cdot 10^{-8}$ m/sec), which means that the descender waterflow may take huminic and carbonic acids from the humous soil and these together cause natural contamination.

We can also find antropogene contamination on cultivated lands (eg. artificial manure, plant protective agents, etc.) though we can neglect their effects because borehole Kl is within the hydrogeological protective zone for waterwork.

Testing the Material

Sampling

As it was already discussed in the last chapter, the chemical quality of the groundwater is basically predetermined by the silt fraction of the water-bearing detritus. (Our study does not include the examination of pollutants carried by the ground water.)

In case of the usual drilling methods (bailer, washing), when the samples are lifted out from under the static level of the ground water, the silt-fraction usually leaks out together with the water. Thus the water-chemical and hydraulic parameters of these samples are not complete.

The sampling method which will satisfy our needs is the following: The samples are taken by means of a sludger, than are placed in a bail where sand, pebbles, silt and water will be together. After settling for several hours the surplus water will be poured off. So the solid phase will be left behind, which will be packed air- and water-tight. Every sample will weight 6 – 10 kg!

It is probable that even these samples will not entirely represent the layer, but a more efficient method could only be adopted by means of refrigeration.

Preparation of the sample, separation

During the investigation we classified the samples according to their grain-size. The grains were selected by dry screening and sieving in the case of grains less than 50 μm in diameter. The fraction, where the grain size was between 50 – 20 μm in diameter, was separated by wet sieving, and if the grain size was even smaller we adopted decantation.

At the fraction where grains were bigger than 50 μm in diameter, we tried to remove the surfaceactive grains by means of clarification. Before the sludge analysis (Stokes-rule) aluminium sulphate or protective colloid water glass was added (coagulation or dispergation) to each sample. When using these two methods together (one after the other), the efficiency of the separation was about 60 – 70 percent only.

During our previous investigations (in the area of Szigetszentmiklós, Tököl, Ráckeve) it became clear, that though the elements of the so-called heavy minerals (magnetite, garnet, zircon, tourmaline etc.) and the melanocratic rockforming minerals (pyroxene, hornblende, biotite, etc.) accumulate in the rocks of the reservoir (transported or not transported), the speed of the weathering of these minerals in the ground water is so small comparing with the length of time the water exploitation takes, that the concentration of their elements is negligible here. For this reason we did not separate these minerals but learned their effects from the data of the water-bearing rock formations.

We similary considered the effects of the andesite, limestone and dolomite grains of the gravel and coarse-sand fraction, i.e. we examined the soluble amount together, without separation.

Examination of the samples

The separation methods discussed in former chapter (screening, dry and wet sieving, sedimentation) were not only good for separation but also gave information about the properties of the material itself. We can also mention that we could not adopt the Atterberg-Köhn and hydrometer analysis at the $d < 50$ μm fraction, because we had too small samples at disposal. On the other hand the amount of the samples were too much to use sedimentation balance so we adopted a procedure that had been worked out in our department. In this procedure the slurry is filled into a glass cell and the temporal change of the extinction is measured. Even if we can get a result using for calculation the Stokes' rule in dealing with photomeric records, the comparison with standards has been found more reliable.

The mineralogical composition was determined by means of combined methods, since we did not know a specific method, which alone would be suitable to determine each mineral in any concentration. The most important method we used was derivatography (suitable for detecting clay minerals, carbonates, sulphide (and X-ray diffraction) for detecting silicates – except phyllosilicates –, quartz, feldspar). Additionally we made optical tests with polarizing microscope and, in case it was necessary, we also made more simple mineralogical examinations (measurement of hardness, density, refraction of light, etc.).

The first step of the chemical examinations was to determine the concentration of the potentially soluble iron and manganese. Since not only oxides, carbonates, sulphides, but also silicates are present among these ions we had to adopt alkaline treatment instead of acidic. We put the samples in a crucible made of platinum or high – alloy steel, added anhydrous Na_2CO_3 to it and melted it in Bunsen flame. So the melted material became acidophile. After evaporation and dissolving in distilled water, we used the usual water-analytical methods. Along the traditional titration we also adopted electrochemical, photometrical, colorimetrical and microchemical reactions. The last one is often used in mineralogical analysis.

We described the plasticity of the clayish rocks on both the over-, and underlying bed-sides with the Atterberger's plasticity coefficient (known as Ip in the soil mechanics).

The ion-exchanger absorption capacity, known as one of the best index numbers for the characterization of surfaces activity, was determined by ammonium-ion exchange and retitration.

The porosity of the samples was counted from their volumes, weights and average specific gravity.

The descendent seepage water of the overlying bed may sontain humic acid and free carbonic acid, therefore we examined a special solution sequence, where the ground water solving material was saturated with CO_2 and humic acid (extracted from peat). However the concentration of such solutions in the nature are smaller, so the results we obtained in the laboratory are maximum values, and are always bigger than in the nature.

The best way to imitate natural conditions is to study solutions made of natural ground water. The speed of convection is slow in the bank-filtration aquifers; this can be imitated either in statical situation, which is similar to dead water condition, or within slow convection, that is, circulation.

The second one has a disadvantage that we cannot disregard the possibility that ground water contacts oxygene (i. e. air), therefore the actual redox potential of the solving material is bigger than that of the ground water. Besides, it is hard to stabilize the CO_2 content on the given level.

Iron and manganese is best dissolved by dead water, and calcium magnesium is best dissolved by circulated water, but the difference is small and considering other factors of certainty, we gave a standard value for the solubility of the ground water.

Evaluation of the results

It is very remarkable that the analytical results have a deviation even in the case of a single well. (We could see this at each (20) previous examinations of the similar purpose.

This is probably due to the genetic inhomogeneity of the reservoir which is in correlation with both the grain distribution and the chemical conditions.

The underlying, water-bearing and overlying layers are essentially the same in each well, only their quantity is different. Neither chemical parameters nor other data do not explain the difference in water quality between the well K1 and the other wells, but peculiarly, their joint effect has this tendency.

We think that the depth of the underlying layer and the thickness of the water-bearing layer is very important at the different wells but there is no significant difference in the thickness of the overlying layer.

	K1	K2	F14
depth of the underlying	24.6	19.8	17.5
layer below the surface in metres	25.8	20.7	17.9
thickness of the waterbearing layer in metres	20.5	16.1	14.4

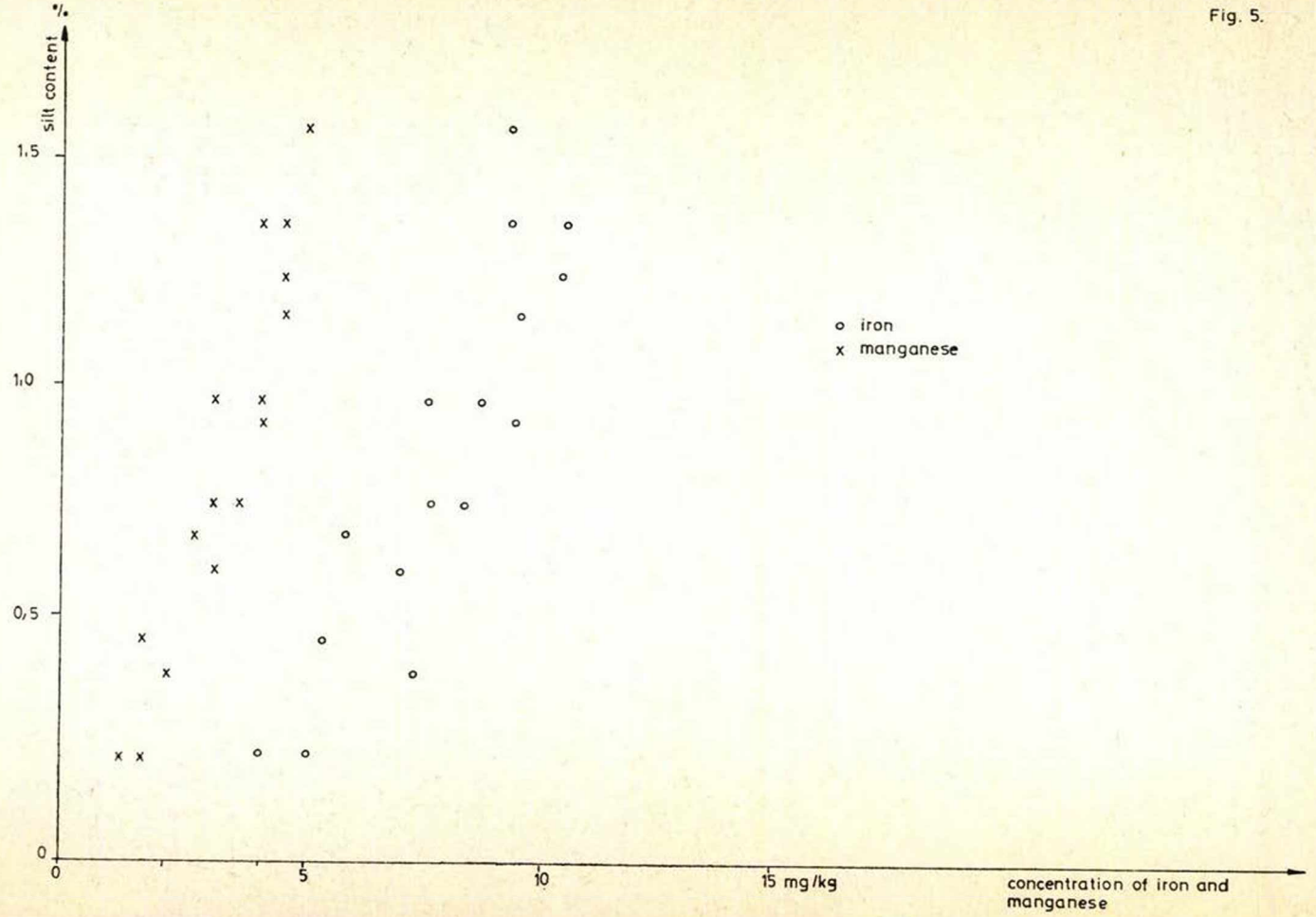
Where the water-bearing layer is thick the effect of the overlying and underlying layer has relatively less importance; the deeper the underlying layer is the less it is outwashed by the slow currents in the ground water.

On the upper part of the underlying layer of the well K1 (between 24.6 – 26.2 m – our sample is from 25.8 m) we can find grey clay of different characteristics than the other, which we think is of great importance. It contains far less pyrite and carbonate than the lower parts of the same well or the underlying layer of the other wells.

There is also a remarkable difference concerning grain-distribution. The water soluble coating is on the surface of the gravel and sand grains, thus the amount of the solved matter depends on the extent of the surface

Connection between silt-content of gravelly sand and contcentration of iron and manganese

Fig. 5.



and not on the weight of the grains as our previous examination had shown. The smaller the grain size the bigger the specific surface is.

There is an obvious correlation with the relative amount of the mud content *(Fig. 5)*. Ions are accumulating on the grains of the mud-fraction (clay mineral and detritus) by ion exchange and adsorption. Besides, this fraction offers favourable conditions for bacteria. Because of the coating the process of solution takes a long time and is reversible. There were essentially the same amount of soluble ions in the silt fraction, which is plausible if we know the material. It is probably because at those processes where ion exchange or adsorption result a balance, this balance will set in at a smaller level if the soluted ion concentration of the ground water is small. Therefore we can conclude that it is not the quality but the quantity of the mud-fraction that is determinant in our case.

Processes in the aquifer

The effect of descendant water

Since the CO_2 concentration of the soil is about 60 times as much as that of the air, the infiltrated precipitation is saturated with CO_2 in the A+B zone of the soil. The speed of the infiltrating water is so slow that its dwelling time is long enough for all the possible chemical reactions. Thus the water dissolved the solid $CaCO_3$ phase of the overlying alluvial clay (originally it also contains loess) in the form of $Ca(HCO_3)_2$– which also contributes to the varying hardness of the ground water.

Huminic acid is washed out from the soil and forms (as humate) chelate complexes with several alkaline earth metals and siderophil elements. This reaction is very important because this is the counterpart of the reversible process. The decomposition is slow and if eg. the concentration is small the dissolved oxygene can not oxidize iron! Huminic acid is able to form protective colloide around the ions even without chemical reaction. Because of this, the occasional putwashing and those chemical reactions which would result solid phase, will become slower and last longer.

The effect of the impervious underlying layer

The outwashed Pannonian Clay contains a relatively big amount of accessory matter like eg. stream sand and loess (eroded from the surrounding hills). Because of its loess content the Pannonian Clay contains a lot of $CaCO_3$, mainly in the form of calcareous nodules. On the other hand even its ferro-sulphide content is washed out.

Ferro-sulphide occures sometimes in the form of crystallized pyrite or marcasite, but more often it appears as less crystallized, almost colloidal, melnikovite ($FeS_2 \cdot nH_2O$) and hydrotroilite ($FeS \cdot nH_2O$). Because of the oxygene-bearing water they oxidize easily. Sulphate is oxidized into sulphuric acid (Thiobacillus ferrooxidans) by the participating bacteria,where there is 2 – 6 pH. This sulphuric acid forms gypsum with the calcium or liquid salt with the magnesium in statu nascendi. Depending on the speed

of the ground water (directly above the aquifer) they get into the aquifer, so the deeper the underlying layer is, the bigger the outwashing will be. Though this is only a very little difference, these effects together may strenghten or weaken each other.

Summary of the hydrochemical process

Huminic acid and $Ca(HCO_3)$ (and artifical manure, plant protective agents and other antropogene materials we will not take any notice of) can get into the aquifer from above and $Ca(HCO_3)_2$, $Mg(HCO_3)_2$?, $Fe(HCO_3)_2$, $Fe(OH)_2$?, $CaSO_4 \cdot nH_2O$, $MgSO_4$, $Mn(HCO_3)_2$?, $Mn(OH_2)$?, H_2SO_4? from below.

Depending on the accessory CO_2 content $Ca(HCO_3)$ remains dissolved or separates as a solid matter. This process is reversible. The solubility of $CaCO_3$, is at about 100 mg/liter, so it is in a permanent balance. The solubility of the Mg–Ca carbonate ("dolomite") is at about 300 mg/litre, so if there is enough dissolvable material the hardness will be chaging at a remarkable rate without any special solvent effect.

The solubility of $CaSO_4 \cdot 2H_2O$ (crystal phase) is 2600 mg/litre, that means about 975 mg/litre SO_4^{2-} ! In the ground water $MgSO_4$ can be dissolved completely. This gives the main part of the hardness and the sulphate content.

The ferro – and ferri – forms of iron transform reversibly, depending on the actual redox potential, which is measured to be +150 – +400 mV instead of +770 mV. The difference is due to the formal-potentials and mainly to bacterial processes. Those bacteria that oxidize iron (Gallionella, Leptothrix, Cladothrix, Clenothrix genera) do that along with Corg consumption, which means that $Fe(OH)_3$ will be precipitated. This precipitation takes part in the reversible processes, so it is reducible. But more often the case is, that bacteria fix this precipitation in their bodies, and it can only be released after the decay of the bacteria and the decomposition of the biomass. It is usually released in dissolved form because of the reductive environment.

Manganese is similar to iron in this respect.

The examination of the samples from the observational wells on Csepel gave similar results, though the thickness of the aquifer is the same at the different wells there, thus the differences in the water-chemical parameters and in the mud fraction of the water-bearing rock gave an obvious correlation.

Summary

The origin of the iron and manganese ions can be explained, if we take complete samples and make more investigation.

Sulphate originates from the oxidation of the ferro-sulphide content (partly bacterial) of the underlying layer.

Iron is released during the same oxidization, and similarly to the manganese, it also becomes mobile. Because of the spontaneous dissolving of the

carbonate the changing hardness of the water will be bigger with 40 mg/litre. Furthermore, if CO_2 is present, dissolved $Ca(HCO_3)_2$ will also cause hardness.

The sulphuric acid (from the oxidation of the pyrite) and calcium form gypsum, which is far more soluble than its concentration in the ground water would indicate.

Magnesium originates from the dissolving of dolomite pebbles and from the carbonate content of the loess in the overlying and underlying layers. The solubility is determined by the CO_2 balance. Together with sulphate it dissolves completely.

We cannot explain the origin of chloride ions with the erosion of minerals, but their amount is basically similar to their concentration in the river; only some 2 – 4 times more than that.

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